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A study of diesel PM with X-ray microspectroscopy

Artur Braun[a,*], Naresh Shah[a], Frank E. Huggins[a], Gerald P. Huffman[a], Sue Wirick[b], Christopher Jacobsen[b], Kerry Kelly[c], Adel F. Sarofim[c]

[a]*Consortium for Fossil Fuel Science, University of Kentucky, Whalen Bldg. Suite 107, 533 South Limestone Street, Lexington, KY 40506, USA*
[b]*Department of Physics and Astronomy, SUNY at Stony Brook, Stony Brook, NY 11794-3800, USA*
[c]*Department of Chemical and Fuels Engineering, Kennecott Research Center, University of Utah, 1495 East 100 South, Room 105, Salt Lake City, UT 84112-1114, USA*

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Abstract

Carbonaceous particulate matter from diesel fuel combustion was studied with Scanning Transmission X-ray Microspectroscopy, a novel synchrotron radiation-based technique, which combines X-ray absorption spectroscopy and microscopy. Single soot particles were chemically identified with a spatial resolution of better than 100 nm. Near-edge X-ray Absorption Fine Structure spectra from the carbon K-absorption edge could be assigned to specific particle regions, making it possible to distinguish graphitic carbon in the soot particles from hydrocarbons, such as residual lubricating oil and diesel fuel and their reaction products.

Keywords: Soot; X-ray absorption; Fine particulate matter; Particle analysis

1. Introduction

The application of novel analytical techniques to fine particulate matter (PM) has gained new importance since the United States Environmental Protection Agency identified PM smaller than 2.5 μm ($PM_{2.5}$) as a key issue for air quality [1,2]. Carbonaceous PM typically constitutes 25–50% of $PM_{2.5}$ in the US, and PM emitted by diesel engines is a major source of diesel PM [2].

From a forensic point of view, detailed knowledge about size, shape and chemical speciation of diesel soot particles is important to (a) understand their impact on the human body and (b) to be able to identify them in PM samples collected from the ambient atmosphere (source attribution) and carry out a source assignment. From an automotive engineering point of view, such information may also be useful for understanding the interaction of diesel soot particles with pollution abatement devices [3].

This paper presents the first application to diesel PM engine exhaust of a promising technique that combines X-ray absorption spectroscopy and X-ray microscopy: scanning transmission X-ray microspectroscopy (STXM) [4]. STXM employs synchrotron radiation with tunable photon energy so that X-ray absorption spectra can be recorded. Using state-of-the-art Fresnel zone plate technology, the X-ray beam can be focused on the sample, which allows for a spatial resolution of objects approximately 50 nm in mean size. This technique has been successfully applied for the study of microbiological marine samples [5], interstellar carbonaceous dust [6], industrial polymers [7] and fuels [8]. One particular advantage of STXM is that only very minute amounts of material (one particle) are necessary to acquire a quality near-edge X-ray absorption fine structure (NEXAFS) spectrum. The present experiments were carried out at beamline X1A [9,10] at the National Synchrotron Light source in Brookhaven National Laboratory. The STXM microscope at this beamline is specialized for carbonaceous samples.

Carbon has a K-shell absorption edge for X-rays that is located at 285 eV [11]. The X-ray absorption characteristics of carbonaceous materials strongly depend on how the carbon atoms are bound to other atoms. In many cases, NEXAFS spectra can be considered fingerprints of particular carbon compounds. For additional literature, we refer the reader to the textbook NEXAFS Spectroscopy by Stoehr [11], which deals extensively with X-ray spectroscopy of carbonaceous materials.

* Corresponding author. Tel.: +1-859-257-6087; fax: +1-859-257-7215.
E-mail address: artur.braun@alumni.ethz.ch (A. Braun).

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Features of carbon NEXAFS spectra of interest for the current study are as follows: carbon atoms with double C=C bonds (graphite, for instance) exhibit a sharp absorption peak at 285 eV—the result of a $1s \rightarrow \pi^*$ transition. Between 287 and 290 eV, relatively sharp peaks from mixed Rydberg $1s \rightarrow CH^*$ atom resonances occur if C–H bonds are present. The ionization potential of carbon at 290 eV causes a step in the absorption spectrum. At higher X-ray energies, up to 320 eV, so called σ^* shape resonances are found. In the present work, we focus on how STXM can achieve an X-ray optical contrast between regions containing predominantly aromatic or aliphatic carbon species and thus distinguish graphitic soot from residual lubricating oil or unburned diesel fuel, and their hydrocarbon reaction products.

2. Experimental section

Soot was generated in a two-stroke diesel test engine (Model KubotaZ482B, 482 cc displacement, typically 0.8–2.2 l/h fuel consumption, no load, 1200 rpm), with a particle concentration of 4.67 mg/m^3, and collected on a quartz filter. The diesel fuel was a 50:50 mixture of the Chevron/Phillips reference fuels T-22 and U-15, with an average cetane number of 46.7 and 79 ppm sulfur content. The fuel/air ratio was 0.013. The engine lubricant was Havoline 10W30 motor oil. While the total soot sample contained 42.7% extractables, only non-extracted soot was used in the present experiment. To prepare samples for STXM studies, the soot particles were dispersed in acetone and ultrasonicated, and a drop of the soot/acetone solution was put on a silicon nitride sample holder, which had a thickness of 50 nm. Electron microscopy, small angle X-ray scattering studies and light scattering data revealed that the primary soot particles had diameters of about 15 nm and were agglomerated into clusters as large as 80 nm [12]. Due to the low photon energy used for carbon STXM, the combined thickness of the particle and the silicon nitride substrate must be very small to allow for a reasonable percentage of X-ray transmission.

The operation principles of the STXM microscope are well described elsewhere [9,10], but we will briefly review them here. Monochromatic synchrotron radiation is focused by a Fresnel zone plate onto the sample with a beam diameter of only 25 nm. The sample stage is then moved in the *xy*-plane with a piezo scanner, so that a transmission image of the sample can be scanned and recorded. With this set-up, objects as small as 30 nm can be detected [11,13]. The energy of the monochromatic X-ray beam is then increased by 0.1 eV, and another image is recorded. In this way, a stack of images at photon energies ranging from approximately 280 to 300 eV is acquired. The total data acquisition time for stacks with a high-energy resolution may be up to 8 h. The information contained in this three-dimensional data set allows selection of specific regions of the image and detailed analysis of the NEXAFS spectra generated for these regions.

The transmitted X-ray intensity at each point depends on the incident intensity, the linear absorption coefficient, and the thickness of the sample and substrate at this point. The linear absorption coefficient $\mu(E)$ is specific for every chemical element and chemical species and is dependent on the X-ray energy, E. The transmitted intensity is given by $I(E,d) = I_0 \exp(-\mu(E)d)$.

The incident intensity, I_0, is determined by selecting a region on the sample holder that is free of sample material. The NEXAFS spectrum for each region is then obtained by plotting the logarithm of the ratio of the intensity measured at the sample-free region to that measured at the selected sample region versus the X-ray energy: $\mu(E)d = \ln(I_0/I(E,d))$.

To reduce absorption in the optical path and yet allow for convenient non-high vacuum experiments, the microscope is contained in a compartment that is flushed with helium gas during the experiments. To obtain the X-ray energy calibration near the carbon K-edge, the STXM compartment was flushed with a mixture of helium and carbon dioxide (~5 vol%) gas. For reference, carbon NEXAFS spectra of pure graphite, diesel fuel, and lubricating oil (10W40) were used. The latter two spectra were obtained by coating the silicon nitride substrate with a thin film of the materials.

3. Results and discussion

Since small carbon particles are quite transparent to the X-ray beam at energies below the carbon K-shell absorption edge, the diesel PM is essentially invisible in images obtained at such energies. A striking example is shown in Fig. 1, which shows two images of a 4 μm wide agglomeration of diesel soot particles, surrounded by a number of smaller non-carbonaceous particles (probably quartz filter material). The image to the left was scanned below the absorption edge, and the image to the right was scanned above the absorption edge. In the left hand image, only a very faint, diffuse indication of the soot agglomeration can be seen. In contrast, the image on

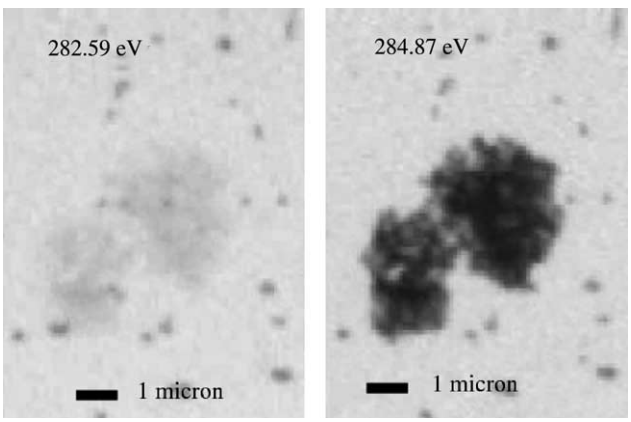

Fig. 1. Sharply contrasting images (6 μm × 7.5 μm) of a diesel PM agglomeration at X-ray energies below (left, 282.59 eV) and above (right, 284.87 eV) the C K-shell absorption edge.

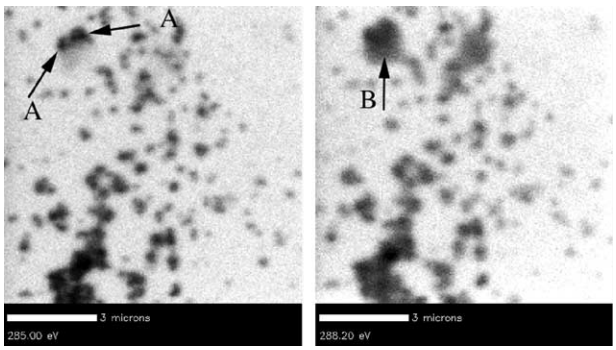

Fig. 2. (a) STXM image (10 μm × 10 μm) of soot particles at 285 eV photon energy. 'A' denotes selected areas for NEXAFS. (b) STXM image (10 μm × 10 μm) of soot particles at 288.2 eV photon energy. 'B' denotes the selected area for NEXAFS.

the right side shows the particle in the center with clear contrast versus the background, while the smaller non-carbonaceous particles appear the same in both images.

Fig. 2 shows two STXM images, obtained from the same sample region at two different X-ray energies. The left image was scanned at photon energy of 285 eV and the right image was scanned at 288.2 eV. Both images show the same distribution of particles, dispersed over an area of about $10 \times 10\ \mu m^2$. However, the particles on the right image appear more diffuse and spread out then the ones in the left image, which appear smaller and sharper.

Two arrows labeled 'A' in the left image point to two particles in a particle agglomeration, with a size of about 0.5 μm each. Both particles can be distinguished in the left image, but not in the right image. Instead, in the corresponding region in the right image, only a large diffuse and dark area can be seen (arrow with label 'B'). This shaded area includes the two particles from 'A', but also material which was hardly visible in the left image. We refer to the part of the dark area, which cannot be linked to the particles in 'A', as the diffuse ring, or region B.

Fig. 3 displays NEXAFS spectra recorded from regions A (particle core) and B (diffuse ring). At 285 eV, carbon has a resonance due to C=C bonds. In the vicinity of 288 eV, there are two hydrocarbon resonances, indicative of C–H bonds. In all diesel soot samples that we have investigated to date, the same resonances have been found. It is reported [11, p. 202] that carbon atoms in an aromatic ring may give rise to such a resonance near 285 eV; however, the energy of the resonance will vary depending on the location of the particular carbon atom in the ring and the atoms to which it is bound.

The NEXAFS from region B has a relatively low intensity at the C=C resonance, whereas the NEXAFS from region A has a pronounced C=C resonance. In region B, the C–H resonances are enhanced relative to the C–H peaks in region A. Therefore, region B, the diffuse area, contains significantly more organic hydrocarbon material than region A, which is the particle core. On the other hand, the particle core contains more material with C=C bonds. Comparison of the spectra in Fig. 3 to those of graphite and the reference diesel fuel in Fig. 4 suggest that the particle core predominantly represents graphitic material, and the diffuse region around the particle core represents volatile organic hydrocarbon derived from unburned diesel fuel and lube oil.

It is worth noting that we have studied larger single diesel PM particles and could assign NEXAFS spectra to the particle cores and particle boundary regions. It was found that C=C bonds were dominant in the particle core regions, while C=C resonances were weak and C–H resonances were enhanced in the particle boundary regions.

It should be noted that the diffuseness of the STXM image obtained at 288.2 eV (2b) may be due in part to a wash-out effect of the acetone used in the sample preparation on diesel fuel and lube oil condensed on the graphitic particle cores. This is supported by Figs. 4 and 5, where the spectrum of a soot particle in a STXM sample prepared dry (spectrum 1) is compared to that of the particle core of the sample prepared using acetone (spectrum 2). These spectra are normalized by setting the intensity of the C=C peak to unity for better comparison. The spectrum of the sample after acetone treatment shows a significantly sharper C=C bond peak than the spectrum of the original

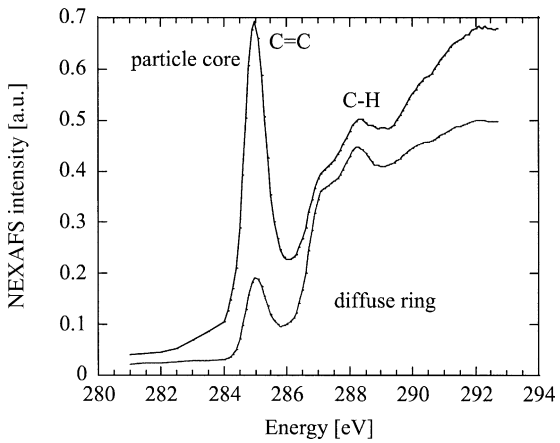

Fig. 3. NEXAFS of particle core and diffuse area.

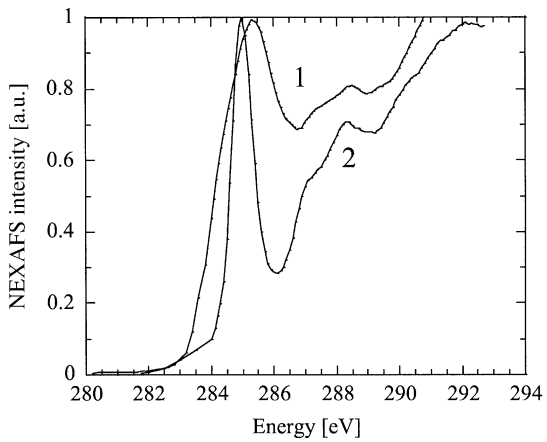

Fig. 4. NEXAFS of particle core before and after acetone leaching.

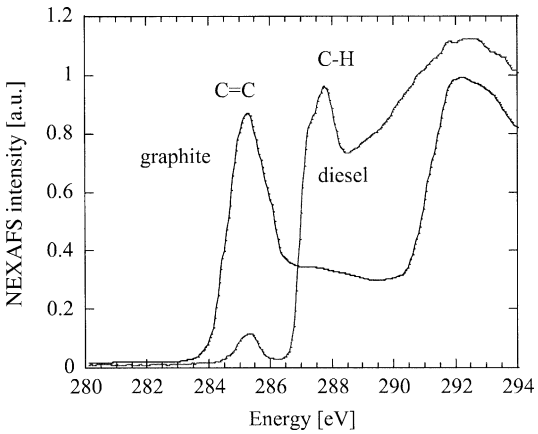

Fig. 5. Reference NEXAFS spectra of graphite and diesel fuel. The graphite spectrum was reproduced from data in [14].

'dry' sample. The intensities of the C–H bond peaks are also weaker for the sample prepared with acetone. This supports the picture that the acetone treatment may leach out volatile organics, which contain more C–H bonds than the graphitic particle core does.

4. Summary and conclusions

This paper presents the first results obtained on diesel soot using a unique synchrotron radiation technique, STXM. It is demonstrated that STXM can identify the molecular structure of carbon in diesel PM with a resolution of approximately 50 nm. Specifically, by identification of regions rich in C=C bonds or C–H bonds, STXM was able to distinguish between graphitic particle cores and regions rich in organic hydrocarbons derived from unburned diesel fuel and lube oil. It was demonstrated that the latter are enriched at particle surfaces and are leached from diesel PM surfaces by acetone used in STXM sample preparation.

These results indicate that STXM is a useful new tool for investigation of the structure of diesel soot and other carbonaceous PM. In a future paper, the results of a more complete study of a suite of diesel PM samples generated from several different fuels under differing load conditions using STXM and other techniques (whole sample NEXAFS, TEM, SEM, XRD, SAXS, etc.) will be presented. Investigations of diesel PM obtained by sampling heavy and light duty truck exhausts and of other types of carbonaceous PM (jet engine emissions, wood smoke) are also underway.

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